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PHASE EQUILIBRIA UP TO THE SOLIDUS LINE IN THE V_2O_5–$Cr_2(MoO_4)_3$ SYSTEM

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Abstract

Phase equilibria being established in the subsolidus area of the V_2O_5–$Cr_2(MoO_4)_3$ system at the whole component concentration range have been studied basing on DTA and X-ray phase powder diffraction. It has been established that the system is not a real two-component system in the subsolidus area. The fact has been proved by the presence of fields in that area, where three solid phases remain in mutual equilibrium.

Keywords: phase equilibria, V_2O_5–$Cr_2(MoO_4)_3$ system

Introduction

Vanadium(V) oxide and chromium(III) molybdate with their interesting catalytic properties are still an object of in-depth study. For that reason it seemed advisable to find out which of the solid phases coexists at equilibrium in the system build by the components at the whole concentration range.

The properties and structure of V_2O_5 are known very well [1–5], and likewise are those of chromium(III) molybdate – the other component of the system under study [6–8].

Experimental

In order to investigate phase equilibria being established in the solid-state V_2O_5–$Cr_2(MoO_4)_3$ system were prepared 18 samples of oxides with compositions corresponding to the whole component concentration range. Mixtures of the oxides with the given compositions were homogenized by grinding, shaped into pastilles and calcinated at conditions dependent on the $Cr_2(MoO_4)_3$ content of the samples expressed in terms of the system components.

Accordingly, samples comprising up to 20.00% mol of $Cr_2(MoO_4)_3$ were heated in the following way:

$$400°C \rightarrow 500°C\ (48\ h) \rightarrow 550°C\ (24\ h\times 2) \rightarrow 570°C\ (24\ h) \rightarrow 590°C\ (24\ h\times 2).$$

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Samples comprising 25.00–50.00% mol of $Cr_2(MoO_4)_3$ were heated, as follows:

400°C → 500°C (48 h) → 550°C (24 h×2) → 570°C (24 h×2).

Samples with the other concentrations of chromium(III) molybdate were heated in the following cycles:

400°C → 500°C (48 h) → 550°C (24 h×2) → 600°C (24 h).

The heating conditions–most favourable for establishment of equilibrium in preparations–were set by screening tests. It was stated that after the above-given heating cycles the preparations reached the equilibrium state. Preliminary investigations were made with samples comprising in their initial mixtures 7.50; 17.50; 30.00; 42.50 and 70.00% mol of $Cr_2(MoO_4)_3$ in terms of the system components.

X-ray phase analysis was made using a diffractometer of a HZG-4/A_2 type with Co radiation and the data listed in PDF cards [9], and those given in the publications [10–12].

Differential thermal analysis (DTA) of the samples at equilibrium was made with a derivatograph, at temperatures 20–1000°C.

Results and discussion

Table 1 shows the compositions of initial mixtures in terms of the system components and X-ray phase analysis of all the preparations at equilibrium. The investigational results show that $Cr_2(MoO_4)_3$ does not remain at a stable equilibrium with V_2O_5. X-ray phase analysis of preparations which contained up to 10.00% mol of $Cr_2(MoO_4)_3$ in their initial mixtures has shown that they are a mixture of two phases, i.e. a solid solution of MoO_3 in V_2O_5 and a solid solution of MoO_3 in $Cr_2V_4O_{13}$. Incorporation of MoO_3 into the crystal lattice of $Cr_2V_4O_{13}$ has also been stated when the phase equilibria being established in the $Cr_2V_4O_{13}$–$CrVMoO_7$ system were studied [13]. In preparations comprising over 10.00% mol of $Cr_2(MoO_4)_3$ occurs a stable phase, $CrVMoO_7$, beside $V_2O_{5(s.s.)}$ and $Cr_2V_4O_{13(s.s.)}$ [11]. These three phases remain in mutual equilibrium only at the $Cr_2(MoO_4)_3$ content of up to 20.00% mol. With the $Cr_2(MoO_4)_3$ content increased to 36.36% mol the mutual equilibrium is being established between $V_2O_{5(s.s.)}$, $CrVMoO_7$ and $V_9Mo_6O_{40}$. A sample comprising 36.36% mol $Cr_2(MoO_4)_3$ at equilibrium is a diphase and it contains $CrVMoO_7$ and $V_9Mo_6O_{40}$, respectively.

Preparations which contained 40.00–50.00% mol of $Cr_2(MoO_4)_3$ in their initial mixtures were mixtures of three phases remaining at equilibrium: $CrVMoO_7$,

Table 1 Composition of initial mixtures and X-ray phase analysis of samples at equilibrium of the V_2O_5–$Cr_2(MoO_4)_3$ system

No.	Composition of initial mixtures in terms of the system components/ %mol		Discovered phases
	$Cr_2(MoO_4)_3$	V_2O_5	
1	2	3	4
1	5.00	95.00	$V_2O_{5(s.s.)}$, $Cr_2V_4O_{13(s.s.)}$
2	7.50	92.50	$V_2O_{5(s.s.)}$, $Cr_2V_4O_{13(s.s.)}$
3	10.00	90.00	$V_2O_{5(s.s.)}$, $Cr_2V_4O_{13(s.s.)}$
4	15.00	85.00	$V_2O_{5(s.s.)}$, $Cr_2V_4O_{13(s.s.)}$, $CrVMoO_7$
5	17.50	82.50	$V_2O_{5(s.s.)}$, $CrVMoO_7$, $Cr_2V_4O_{13(s.s.)}$
6	20.00	80.00	$CrVMoO_7$, $V_2O_{5(s.s.)}$, $Cr_2V_4O_{13(s.s.)}$
7	25.00	75.00	$CrVMoO_7$, $V_2O_{5(s.s.)}$, $V_9Mo_6O_{40}$
8	30.00	70.00	$CrVMoO_7$,$V_9Mo_6O_{40}$, $V_2O_{5(s.s.)}$
9	35.00	65.00	$CrVMoO_7$,$V_9Mo_6O_{40}$, $V_2O_{5(s.s.)}$
10	36.36	63.64	$V_9Mo_6O_{40}$, $CrVMoO_7$
11	40.00	60.00	$V_9Mo_6O_{40}$, $CrVMoO_7$, MoO_3
12	42.50	57.50	$V_9Mo_6O_{40}$, $CrVMoO_7$, MoO_3
13	45.00	55.00	$CrVMoO_7$,MoO_3, $V_9Mo_6O_{40}$
14	50.00	50.00	MoO_3, $CrVMoO_7$
15	60.00	40.00	MoO_3, $CrVMoO_7$, $Cr_2(MoO_4)_3$
16	70.00	30.00	MoO_3, $Cr_2(MoO_4)_3$, $CrVMoO_7$
17	80.00	20.00	$Cr_2(MoO_4)_3$, MoO_3, $CrVMoO_7$
18	90.00	10.00	$Cr_2(MoO_4)_3$, MoO_3, $CrVMoO_7$

$V_9Mo_6O_{40}$ and MoO_3, whereas a sample which contained 50.00% mol of $Cr_2(MoO_4)_3$ and 50.00% mol of V_2O_5 in the equilibrium state consisted of two phases only, viz. MoO_3 and $CrVMoO_7$.

X-ray analysis of preparations in equilibrium representing the other component concentration range for the system under study, that is, over 50.00% mol of $Cr_2(MoO_4)_3$, showed three phases: $CrVMoO_7$, MoO_3 and $Cr_2(MoO_4)_3$.

The solid-state phase equilibria at the whole component concentration range in the V_2O_5–$Cr_2(MoO_4)_3$ system have been illustrated in the Fig. 1. The temperature-dependent area of subsolidus line has been determined basing on the onset temperature of the first endothermic effect recorded at the equilibrium state on the DTA curves.

The experimental results imply that the V_2O_5–$Cr_2(MoO_4)_3$ system is not a real two-component system in the subsolidus area at the whole component concentration range.

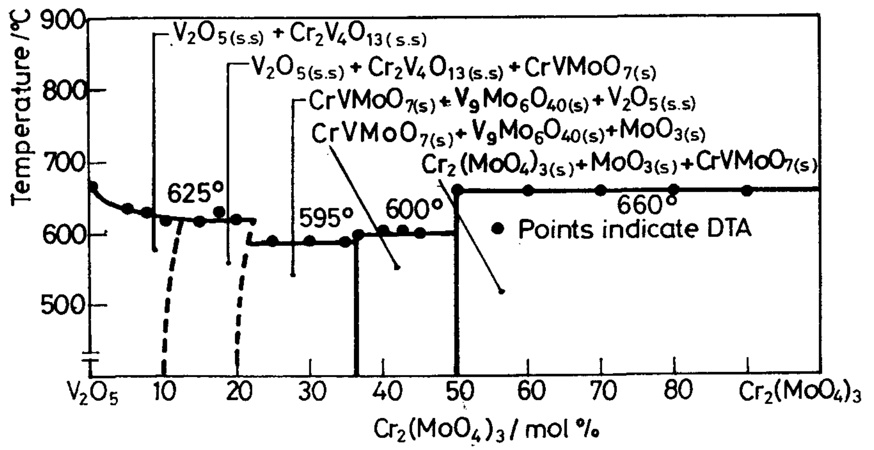

Fig. 1 The diagram of the phase equilibria in the solid-state V_2O_5–$Cr_2(MoO_4)_3$ system; ● measured by DTA

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Zusammenfassung — Auf der Basis von DTA und Röntgenphasenpulverdiffraktion wurde das im subfesten Bereich des Systemes V_2O_5–$Cr_2(MoO_4)_3$ festgestellte Phasengleichgewicht über den gesamten Konzentrationsbereich der Komponenten untersucht. Man stellte fest, daß das System in diesem Bereich kein tatsächliches Zweikomponentensystem ist. Dieser Umstand wurde dadurch bewiesen, daß in einigen Regionen dieses Bereiches drei verschiedene Festphasen im Gleichgewicht zueinander stehen.